π-ELECTRON STRUCTURE OF THE NITROFURAN SYSTEM

II.* MOLECULAR ORBITALS OF THE π ELECTRONS OF 5-NITROFURAN AND ITS 2-SUBSTITUTED DERIVATIVES

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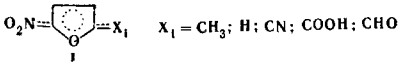
The Hückel MO method was used to calculate the molecular orbital systems of the π electrons of 5-nitrofuran, 2-methyl-5-nitrofuran, 2-cyano-5-nitrofuran, 5-nitropyromucic acid, and 5-nitro-2-furfural molecules. The MO of these compounds were compared with the MO of the corresponding benzene analogs. The calculated data are in good agreement with experimental data obtained by means of EPR, IR, and UV spectroscopy. The linear dependence of the long-wave maximum in the electronic spectra on the difference in the frontal levels has a slope (β) of $-18 \cdot 10^3$ cm^{-1} (52 kcal·mole^{-1}).

The results (presented in [1, 2]) of a quantum-chemical calculation of the density of the unpaired electron in anion radicals of the 5-nitrofuran series are a partial result of our Hückel MO LCAO calculation of the system of MO of the π electrons of 5-nitrofuran and its derivatives (I):

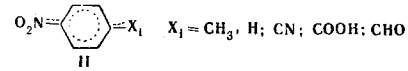


I

In this communication we present the complete calculated systems of the π-electron MO of I in the form of matrixes of the cjr coefficients and the mj parameters corresponding to the energy levels (Tables 1-5); these are compared with the experimental data from a spectroscopic study of 5-nitrofurans. The method used to calculate the Hückel MO (HMO) and the parameters selected are described in [1].

The validity of the calculation of the HMO of I has already been confirmed by the good agreement between the parameters obtained and the polarographic half-wave potentials and the hfs constants of the EPR spectra of the corresponding anion radicals of I [2]. In this study we were able to show that the examined models of the π-electron systems quite satisfactorily also explain the character of the electronic and IR spectra of I. The data for comparison were taken in part from [3-6] and were also obtained in part from our experiments.

To compare the π-electron structure of the 5-nitrofurans with the structure of the corresponding nitrobenzene derivatives we carried out similar HMO calculations for system II using the same parameters for the X_i substituents:



II

The calculated electron densities and bond orders for series I and II are compared in Tables 6-8. A comparison of the electron densities in the last occupied MO in the nitrofurans and nitrobenzenes makes it possible to conclude that the furan ring is capable of giving up electrons more readily than the benzene ring. However, comparing the electron-density distribution in the anion radicals of series I and II we see that the

*See [1] for communication I.

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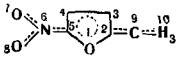
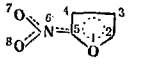
TABLE 1. Energy-Level Parameters (m_j) and Coefficients (c_j) Calculated by the HMO Method for I



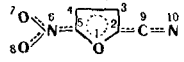
										m_j
−0,0029	0,2562	−0,1153	0,0419	−0,0117	0,0036	−0,0014	−0,0014	−0,6737	0,6815	−2,971
−0,0487	−0,2177	0,4272	−0,5668	0,5531	−0,2798	0,1427	0,1427	−0,0707	0,1286	−1,875
0,1545	−0,5264	0,5199	−0,0289	−0,3925	0,3510	−0,2214	−0,2214	−0,0657	0,2197	−1,248
0,1257	−0,3892	0,0543	0,4562	−0,1961	−0,4540	0,4229	0,4229	0,0060	0,1394	−0,393
−0,0076	−0,5170	−0,4317	0,2801	0,5388	0,0836	−0,2288	−0,2288	0,1170	0,2280	0,790
0	0	0	0	0	0	0,7071	−0,7071	0	0	1,400
0,3081	−0,2173	−0,5536	−0,6080	−0,3314	0,0083	0,1174	0,1174	0,1321	0,1637	1,517
−0,3169	0,2300	0,1185	0,0106	−0,0751	0,0163	0,0278	0,0278	0,6855	0,5960	2,376
−0,8670	−0,3008	−0,1535	−0,1230	−0,1963	0,0966	0,0960	0,0960	−0,1886	−0,1317	3,081
−0,1006	−0,0218	−0,0206	−0,0683	−0,2392	−0,7588	−0,4191	−0,4191	−0,0060	−0,0031	4,423

TABLE 2



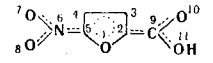
								m_j
−0,0384	−0,2708	0,4559	−0,5659	0,5366	−0,2685	0,1362	−0,1362	−1,892
−0,1624	0,5571	−0,5139	0,0014	0,4166	−0,3565	0,2220	0,2220	−1,282
0,1275	−0,3936	0,0586	0,4519	−0,2000	−0,4577	0,4269	0,4269	−0,391
−0,0023	−0,5538	−0,3981	0,3278	0,5600	0,0763	−0,2321	−0,2321	0,851
0	0	0	0	0	0	−0,7071	0,7071	1,400
−0,3422	0,3009	0,5889	0,5836	0,2896	−0,0094	−0,1022	−0,1022	1,554
0,9104	0,2525	0,1375	0,1247	0,2040	−0,0975	−0,0995	−0,0995	3,037
0,1000	0,0204	0,0202	0,0682	0,2391	0,7589	0,4192	0,4192	4,423

TABLE 3



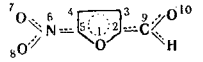
										m_j
−0,0351	0,4819	−0,4196	0,3217	−0,2290	0,1020	−0,0488	−0,0488	−0,5438	0,3518	−2,091
0,1050	−0,1391	−0,1627	0,4688	−0,5660	0,3099	−0,1639	−0,1639	0,4072	−0,2955	−1,758
−0,1125	0,3492	−0,5264	0,1547	0,2888	−0,3460	0,2344	0,2344	0,3601	−0,3488	−1,065
−0,1357	0,3870	−0,1366	−0,4269	0,2350	0,4279	−0,4101	−0,4101	0,1320	−0,1967	−0,342
0,0017	0,5401	0,3798	−0,3238	−0,5448	−0,0728	0,2250	0,2250	0,0166	−0,2359	0,860
0	0	0	0	0	0	0,7071	−0,7071	0	0	1,400
0,3297	−0,2736	−0,5753	−0,5883	−0,3010	0,0091	0,1064	0,1064	0,0422	0,1557	1,543
0,3692	−0,1257	−0,0477	0,0234	0,0912	−0,0269	−0,0363	−0,0363	−0,5784	−0,7063	2,638
0,8376	0,3066	0,1542	0,1200	0,1890	−0,0944	−0,0931	−0,0931	0,2335	0,2232	3,093
−0,1006	−0,0218	−0,0206	−0,0683	−0,2392	−0,7588	−0,4191	−0,4191	−0,0063	−0,0035	4,423

TABLE 4



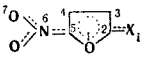
											m_j
−0,0130	0,4590	−0,4891	0,4523	−0,3669	0,1725	−0,0849	−0,0849	−0,3667	0,1679	0,0625	−1,995
0,1360	−0,3668	0,0671	0,3359	−0,5229	0,3116	−0,1709	−0,1709	0,4824	−0,2454	−0,0888	−1,645
−0,0712	0,1799	−0,4824	0,2385	0,2076	−0,3533	0,2549	0,2549	0,5021	−0,3327	−0,1111	−0,915
−0,1402	0,3696	−0,2026	−0,3918	0,2631	0,3980	−0,3919	−0,3919	0,2476	−0,2206	−0,0661	−0,296
0	−0,5443	−0,3458	0,3459	0,5443	0,0667	−0,2216	−0,2216	−0,0891	0,2365	0,0395	0,897
0	0	0	0	0	0	0,7071	−0,7071	0	0	0	1,400
0,3360	−0,2933	−0,5794	−0,5765	−0,2873	0,0093	0,1014	0,1014	0,0057	0,1725	−0,0040	1,553
0,1441	−0,1272	−0,0725	−0,0142	0,0318	−0,0059	−0,0115	−0,0115	−0,3308	−0,6965	0,6015	2,260
−0,7965	−0,1662	−0,0991	−0,1046	−0,1851	0,0820	0,0860	0,0860	0,1649	0,1768	0,4505	2,993
−0,4224	−0,2433	−0,1085	−0,0656	−0,0909	0,0538	0,0492	0,0492	−0,4181	−0,3877	−0,6365	3,225
−0,1006	−0,0219	−0,0207	−0,0683	−0,2392	−0,7588	−0,4191	−0,4191	−0,0062	−0,0034	−0,0029	4,423

TABLE 5

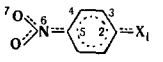


										m_j
−0,0069	0,4433	−0,4948	0,4753	−0,3946	0,1873	−0,0926	−0,0926	−0,3209	0,1476	−1,979
0,1426	−0,4148	0,1254	0,2994	−0,5109	0,3129	−0,1735	−0,1735	0,4732	−0,2433	−1,612
0,0569	−0,1246	0,4599	−0,2625	−0,1812	0,3576	−0,2634	−0,2634	−0,5247	0,3547	−0,868
0,1403	−0,3602	0,2207	0,3782	−0,2696	−0,3864	0,3839	0,3839	−0,2804	0,2519	−0,281
0,0001	0,5427	0,3419	−0,3466	−0,5425	−0,0660	0,2206	0,2206	0,0945	−0,2521	0,900
0	0	0	0	0	0	−0,7071	0,7071	0	0	1,400
−0,3362	0,2935	0,5796	0,5767	0,2874	−0,0093	−0,1014	−0,1014	−0,0056	−0,1705	1,553
−0,3055	0,1291	0,0535	−0,0146	−0,0755	0,0209	0,0295	0,0295	0,5257	0,7763	2,584
0,8604	0,2973	0,1519	0,1220	0,1949	−0,0958	−0,0953	−0,0953	0,1833	0,1857	3,080
−0,1005	−0,0217	−0,0206	−0,0683	−0,2392	−0,7588	−0,4191	−0,4191	−0,0055	−0,0030	4,423

TABLE 6. Electron Densities (e_r) in Series I and II



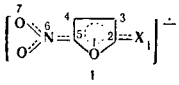
I



II

X_i		e_1	e_2	e_3	e_4	e_5	e_6	e_7
CH_3	I	1,914	0,916	1,062	0,936	1,002	1,186	1,504
	II		0,950	1,007	0,953	1,001	1,174	1,486
H	I	1,912	0,923	1,050	0,936	0,997	1,182	1,500
	II		0,956	1,001	0,953	0,996	1,173	1,483
CN	I	1,914	0,954	1,003	0,942	0,977	1,182	1,495
	II		0,976	0,984	0,955	0,983	1,173	1,481
COOH	I	1,913	0,971	0,965	0,944	0,959	1,180	1,490
	II		0,989	0,963	0,957	0,970	1,172	1,478
CHO	I	1,913	0,972	0,958	0,945	0,955	1,180	1,490
	II		0,989	0,960	0,957	0,968	1,172	1,478

TABLE 7. Density of the Unpaired Electron in Anion Radicals of Series I and II



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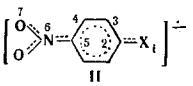
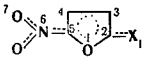


II

X_i		ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	ρ_7
CH_3	I	0,016	0,152	0,003	0,208	0,039	0,206	0,179
	II		0,112	0,005	0,104	0,039	0,223	0,182
H	I	0,016	0,155	0,003	0,212	0,040	0,210	0,182
	II		0,124	0,005	0,105	0,040	0,226	0,195
CN	I	0,018	0,150	0,019	0,182	0,055	0,183	0,168
	II		0,123	0,014	0,095	0,052	0,199	0,180
COOH	I	0,020	0,137	0,041	0,154	0,069	0,158	0,154
	II		0,116	0,026	0,084	0,064	0,173	0,163
CHO	I	0,020	0,130	0,049	0,143	0,073	0,149	0,147
	II		0,111	0,030	0,079	0,067	0,163	0,156

TABLE 8. Bond Orders (p_{rs}) of Series I and II



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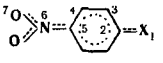

II

X_i		p_{12}	p_{15}	p_{23}	p_{34}	p_{45}	p_{56}	p_{67}
CH_3	I	0,254	0,224	0,835	0,474	0,785	0,412	0,628
	II			0,637	0,686	0,602	0,366	0,640
H	I	0,260	0,228	0,866	0,463	0,790	0,402	0,622
	II			0,656	0,680	0,606	0,373	0,637
CN	I	0,247	0,232	0,833	0,469	0,789	0,396	0,625
	II			0,633	0,683	0,605	0,370	0,637
COOH	I	0,241	0,236	0,822	0,469	0,790	0,389	0,628
	II			0,625	0,683	0,606	0,367	0,639
CHO	I	0,240	0,237	0,817	0,469	0,802	0,389	0,628
	II			0,622	0,684	0,606	0,377	0,636

furan ring also has a greater affinity for taking on electrons than the benzene ring (Table 7). The 4 position of the 5-nitrofuran molecules has the maximum electrophilicity (Table 7). As one would expect, the electron density within the limits of the nitro group is shifted markedly toward the oxygen atoms (Table 6). The π-electron system of 5-nitrofuran is more mobile than that of nitrobenzene; changes in the electron-accepting properties of the X_i substituent are reflected in the electron densities and bond orders to a greater extent in series I than in series II. As the electron-acceptor properties of X_i increase, the π-electron distribution

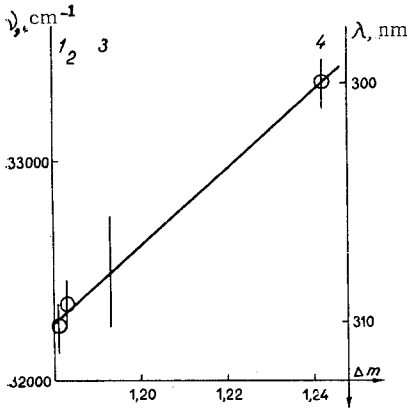

Fig. 1

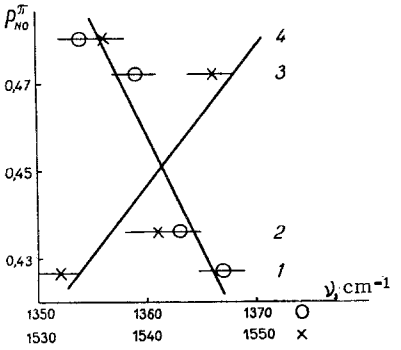

Fig. 2

Fig. 1. Dependence of the frequencies (ν) of the first $\pi'-\pi^*$ transition in 2-X_i-5-nitrofurans on the difference in the frontal level energies calculated by the HMO method (Δm): 1) $X_i = CHO$; 2) $X_i = CH_3$; 3) $X_i = COOH$; 4) $X_i = H$.

Fig. 2. Comparison of the frequencies of the valence symmetrical (○) and antisymmetrical (×) vibrations (ν) of the nitro group in 2-X_i-5-nitrofurans and of the nitro-group bond orders ($p_{NO\pi}$): 1) $X_i = H$; 2) $X_i = CH_3$; 3) $X_i = COOH$; 4) $X_i = CHO$.

in the diene system of the furan ring approaches that of the benzene ring. The electron deficit on the oxygen atom in the furan ring depends slightly on the nature of X_i. The C–O bond order has the minimum value as compared with the other bonds in the furan ring (Table 8). As the electrophilic properties of the X_i substituents in series I decrease, the 1-2 bond order increases, while the 1-5 bond order decreases.

The electronic spectra of I contain a long-wave absorption band at ~300 nm [4, 5], which is due to a $\pi'-\pi^*$ transition of the electrons from the upper occupied ψ_i MO to the first vacant ψ_{j+1} MO and is associated with an increase in the electron density on the nitro group. In the HMO representation the difference in the energies of the frontal levels [$\Delta E = \beta (m_j - m_{j+1}) = \beta \Delta m$] should correspond to a quantum of energy being absorbed. We have established that these values for I are actually linearly related (Fig. 1) and that the proportionality coefficient (β) is $-18 \cdot 10^3$ cm^{-1} (52 kcal-mole^{-1}), which is close to the value previously found [1] from polarographic data ($\beta = -65$ kcal-mole^{-1}). However, the correlation line presented in Fig. 1 does not pass through the origin; this is completely explainable if one bears in mind that the HMO method does not allow for configuration interaction and singlet-triplet splitting effects [7].

By comparing the calculated order of the $N \overset{\cdots}{-} O$ bond formed by the π electrons in the nitro group of system I (Table 8) and the corresponding normal vibrations in the IR spectra, we see that, as the bond order increases, the frequency of the valence symmetrical vibrations of the nitro group decreases, while the frequency of the valence antisymmetrical vibrations tends to increase (Fig. 2).

To a first approximation the calculated data also agree with the experimental values of the dipole moments of several derivatives of series I [8].

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